Supporting Information

X-ray Spectroscopic Characterization of Co(IV) and Metal-Metal Interactions in Co_4O_4: Electronic Structure Contributions to the Formation of High-Valent States Relevant to the Oxygen Evolution Reaction

Ryan G. Hadt,[†] Dugan Hayes,[†] Casey N. Brodsky,[§] Andrew M. Ullman,[§] Diego. M. Casa,[||] Mary H. Upton,[||] Daniel G. Nocera,*[,§] Lin X. Chen*[,†,‡]

[†] *Chemical Sciences and Engineering Division and the [||] Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439, United States*

[‡] *Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States*

[§] *Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States*

Table of Contents *Page*

A. Experimental Methods

A.1. Synthesis

Syntheses of the neutral (**1**) and singly oxidized (**2**) cubane were performed as described in a previous publication.[1] Synthesis of crude $Co_4O_4(OAc)_4(py)_4$ (crude **1**) was performed according to the procedures of Dismukes[2] and Bonchio.[3] Purification of **1** was performed on a Biotage Isolera One automated flash chromatography system using a mobile phase gradient of 2–10% methanol/dichloromethane. A typical loading ratio was 10 mg of crude material for 1 g of silica. Samples were loaded onto the columns using a minimal volume of dichloromethane. Typical yields after purification were 40–50%. Compound **2** was prepared by chemical oxidation of **1**. Purified **1** (75.5 mg, 0.0886 mmol) was dissolved in 10 mL of acetonitrile. In a separate vial, 1.1 equiv of $(NH_4)_2Ce(IV)(NO_3)_6$ (53.4 mg, 0.0974 mmol) was dissolved in 3 mL of acetonitrile. To a stirring solution of **1** was added the Ce(IV) solution in a dropwise manner. The mixture darkened and was stirred at room temperature for 30 min. The mixture was concentrated under reduced pressure and redissolved in 8 mL of DI water. To this aqueous solution was added a solution of 452 mg of KPF_6 in 5 mL of DI water, which resulted in a precipitation of the product. This precipitate was filtered over a 5 μm nylon filter paper, washed with 10 mL of ice water, and then 20 mL of diethyl ether. The solid was dried under reduced pressure resulting in a dark green solid (66.4 mg, 0.0666 mmol, 75.1 % yield). Characterization of **1** and **2** (^{1}H NMR and mass spectrometry) were consistent with spectra reported in the literature.[1]

A.2. Spectroscopic Methods

A.2.1. Co K-edge X-ray absorption

Co K-edge (~7709 eV) XANES and EXAFS data were collected at beamline 12-BM-B at the Advanced Photon Source of Argonne National Laboratory using a water-cooled, double-crystal, fixed-exit monochromator with Si(111) crystals and a double mirror system (flat plus toroidal) with a cutoff energy of 23 keV to focus the beam to ~0.5 mm (v) × 1 mm (h). All data were collected in transmission mode; in this setup, an ion chamber was placed before the sample for the incident X-ray flux reference signal I^0, and a second and third ion chamber were placed after the sample. A Co foil was inserted between the second and third ion chambers for energy calibration. Data were collected at room temperature on solid powdered samples loaded into a 1 mm aluminum sample holder with Kapton windows. All K-edge XAS measurements were made in a dry nitrogen purged sample compartment mounted on a motor-controlled translational stage. No sample damage due to X-ray beam exposure was observed after multiple scans using the same sample position. Three to five scans, each at different sample positions, have been averaged for analysis. Background subtraction and data normalization were carried out using the Athena software package.[4]

A.2.2. Co L-edge X-ray absorption

Co L-edge (~780 eV) XAS data were collected at beamline 7.0.1 at the Advanced Light Source of Lawrence Berkeley National Laboratory using a variable line spacing plane grating soft X-ray monochromator (VLS PMG) with two gratings (250 and 1000 lines/mm). The X-ray spot size was ~100 × 100 μm. Samples were dissolved in dichloromethane and drop-cast onto 200 nm silicon nitride windows (Norcada) to form thin solid films of ~10 – 20 nm; L-edge XAS data were collected in transmission mode using an ultra-high vacuum sample chamber (~10^{-6} Torr) and a photodiode detector.

A.2.3. X-ray emission and resonant inelastic X-ray scattering

1s3p resonant inelastic X-ray scattering (RIXS) (incident energy tuned to the Co K-edge ~7709 eV) were collected at beamline 27-ID-B at the Advanced Photon Source of Argonne National Laboratory. For high-resolution incident X-ray radiation at the Co K-edge, the incoming radiation was monochromated using a diamond(1,1,1) monochromator. Data were collected at room temperature using the MERIX spectrometer as described in reference 5. The X-ray emission was monochromatized using a Ge(4,4,4) spherical diced analyzer at a 1 m radius. Data at each incident energy was collected on a fresh sample spot, and no evidence of sample degradation occurred over the course of the experiment. The incident energy range spanned 7707 – 7714 eV in 0.5 eV steps. The 1s3p emission was collected in 0.25 eV steps. Data were normalized to the respective pre-edge intensities. The overall resolution of the instrument was ~500 meV, and the incident energy bandwidth was ~482 meV.

A.3. Computational Methods

All DFT calculations were carried out using Gaussian 09,[6] revision A.02, software installed on the Blues or Fusion clusters at Argonne National Laboratory. Molecular orbital compositions were determined using the QMForge program[7] and all orbital surfaces were generated using the β-LUMO program.[8] Geometry optimizations for neutral and delocalized mixed-valence states were carried out using the BP86 functional[9–11] (spin unrestricted for paramagnetic states), in combination with a 6-311G(d)[12–14] basis set on all atoms. This combination was also used for all CoM_3O_4 models (M = Al(III), Ga(III), or Sc(III)). A B(20HF)P86 functional was used for geometry optimizations of the localized Co(IV) state. Frequency calculations and stability checks were carried out to ensure geometries and wavefunctions represented minima. For additional computation benchmarking various B(XXHF)P86 functionals were used, which allowed for mixing of HF exchange from 00 – 25 %. Single point energy calculations and population analyses were carried out using the functionals mentioned above, but with a split basis set (6-311+G(d) for Co, O, and N atoms, and 6-311G(d) for C and H atoms). Solvation effects were included using the polarized continuum model (PCM).[15]

A.4. Electrochemistry

Cyclic voltammograms (CVs) were recorded at ambient temperature using a CH Instruments potentiostat. Compound **1** was dissolved in a nitrogen-purged solution containing a supporting electrolyte, 0.1 M *n*-Bu_4NPF_6 (purchased from Sigma Aldrich, used without any purification and stored under vacuum) in acetonitrile (previously purified and dried by passing through a neutral alumina column under argon) solution. A three-electrode cell configuration was used: the working electrode was a freshly polished glassy carbon (GC) electrode; the counter electrode was a platinum wire; and a silver wire pseudo-reference electrode was used in combination with a ferrocene/ferrocenium internal standard reference. The GC polishing procedure was performed for 2 min on felt using 1 μm diamond paste, with ethanol as a lubricant. After polishing, the electrode was briefly sonicated in ethanol and dried with a stream of compressed air. The ohmic drop was carefully compensated in all electrochemical experiments by using the positive feedback compensation implemented in the instrument.

B. Tables

Table S1. EXAFS fitting parameters.[a]

Atom	N	σ^2 (Å^{-2})	R (Å)[b]
Co(III)			
O(oxo)	3	0.0025	1.87
O(OAc)	2	0.0025	1.96
N(py)	1	0.0025	1.93
Co(1)	2	0.0040	2.73
Co(2)	1	0.0040	2.85
C	2	0.0040	2.86
Co(IV)			
O(oxo)	3	0.0010	1.82
O(OAc)	2	0.0010	1.91
N(py)	1	0.0010	2.00
Co(1)	2	0.0040	2.68
Co(2)	1	0.0040	2.82
C	2	0.0040	2.82

[a] Co(III): E^0 = 2.8 eV; S_0^2 0.7, number of independent points = 10.6, .fitting region: 3.08 ≤ *k* (Å^{-1}) ≤ 11.6, 1 ≤ R(Å) ≤ 3. Co(IV): E^0 =-1.5 eV, S_0^2 = 1.0, number of independent points = 7.1, fitting region: 3.10 ≤ *k* (Å^{-1}) ≤ 9.65, 1 ≤ R(Å) ≤ 2.75.

[b] Distances were set to the DFT distances for Co(III) and Co(IV) localized geometries (from Table S2 below).

Due to the presence of multiple different O/N and Co-Co distances, a full fit to the EXAFS data would be underdetermined and was therefore not carried out; rather, the Co K-edge k^3-weighted EXAFS spectra of neutral **1** and Co(IV) (obtained from the difference XAS spectrum) and their Fourier transforms were modeled using the neutral and localized Co(IV) DFT structures. In these models, the metal-ligand and metal-metal bond distances were kept fixed to the DFT value, and the Debye-Waller factors for first or second shells were kept fixed to their respective values (Table S1). These parameters were able to acceptably reproduce the EXAFS data (see below, Figure S1).

Table S2. Selected bond distances from X-ray crystallography and computational models.

Bond	Co_4O_4[a]	Co_4O_4[b]	N(calc)[c]	O(calc)[c]	O(calc)[d]
Co(1)-Co(2)	2.81	2.89	2.85	2.86	2.83
Co(3)-Co(4)	2.82	2.81	2.85	2.86	2.82
Co(1)-Co(4)	2.70	2.71	2.73	2.70	2.68
Co(1)-Co(3)	2.70	2.73	2.73	2.70	2.68
Co(2)-Co(4)	2.70	2.71	2.73	2.70	2.70
Co(2)-Co(3)	2.71	2.73	2.73	2.70	2.71
Co(1)-N	1.95	1.96	1.93	1.95	2.00
Co(2)-N	1.96	1.96	1.93	1.95	1.97
Co(3)-N	1.97	1.92	1.92	1.95	1.93
Co(4)-N	1.97	1.95	1.93	1.95	1.93
Co(1)-OAc(1)	1.95	1.96	1.96	1.95	1.92
Co(1)-OAc(2)	1.95	1.90	1.96	1.94	1.91
Co(1)-O(1)	1.87	1.91	1.87	1.87	1.82
Co(1)-O(2)	1.84	1.88	1.87	1.87	1.83
Co(1)-O(3)	1.89	1.86	1.87	1.87	1.81
Co(2)-OAc(1)	1.95	1.96	1.96	1.94	1.91
Co(2)-OAc(2)	1.96	1.91	1.96	1.94	1.92
Co(2)-O(1)	1.87	1.91	1.87	1.87	1.88
Co(2)-O(2)	1.86	1.88	1.87	1.87	1.87
Co(2)-O(3)	1.86	1.87	1.87	1.87	1.85
Co(3)-OAc(1)	1.98	1.95	1.96	1.94	1.94
Co(3)-OAc(2)	1.94	1.95	1.96	1.94	1.91
Co(3)-O(1)	1.87	1.87	1.87	1.87	1.87
Co(3)-O(2)	1.85	1.86	1.87	1.87	1.85
Co(3)-O(3)	1.87	1.87	1.87	1.86	1.87
Co(4)-OAc(1)	1.97	1.93	1.96	1.94	1.94
Co(4)-OAc(2)	1.93	1.94	1.96	1.94	1.91
Co(4)-O(1)	1.88	1.86	1.87	1.87	1.87
Co(4)-O(2)	1.85	1.86	1.87	1.87	1.85
Co(4)-O(3)	1.87	1.91	1.87	1.87	1.87

[a] Neutral structure; reference 16. [b] Oxidized structure (PF_6 salt); reference 17. [c] BP86/6-311-G(d) optimized
[d] BP86(20HF)/6-311-G(d) optimized (localized Co(IV))

Table S3. Relative energies of the delocalized and localized states of the Co_4O_4 cubane.

% HF	ΔE (kcal/mol)[a]
0	–9.2
5	–6.7
10	–4.1
15	–0.3
20	5.5
25	11.9

[a] Energy difference is defined as energy(delocalized) – energy(localized); thus, the localized wavefunction becomes the ground state for values of HF exchange > ~15 %.

Table S4. Mulliken population analyses of the β-LUMO of the Co_4O_4 cluster using different amounts of HF exchange. Gas phase.[a]

%HF	Del [b]		IE (eV)	$E^0(1)$ [c]	Loc [d]				IE (eV)	$E^0(1)$ [c]
	Co(d)[e]	*O(p)*[e]			*Co(d)*[e]	*O(p)*[e]	*Co(d)*[f]	*Co(d)*[g]		
0	70.1	19.1	5.27	0.83	24.8	19.3	44.5	69.3	5.61	1.12
5	68.3	20.9	5.47	1.03	28.1	20.9	39.7	67.8	5.70	1.26
10	66.1	23.0	5.70	1.26	35.9	22.0	30.6	66.5	5.82	1.38
15	63.3	25.4	5.96	1.52	60.2	17.7	11.1	71.3	5.93	1.49
20	59.9	28.1	6.24	1.80	74.4	10.8	4.7	79.1	5.96	1.52
25	55.9	31.3	6.52	2.08	77.2	9.9	3.3	80.5	5.98	1.54

[a] BP86/6-311G(d) optimized geometries. [b] Delocalized geometric and electronic structure. [c] V vs. NHE. [d] Localized geometric and electronic structure. [e] BP86(XXHF)/6-311+G(d)/6-31G(d) population analyses; total d or p characters are given. [f] 'Spectator Co(III)' contribution. [g] Total Co(d) character including 'spectator Co(III)'.

Table S5. Mulliken population analyses of the β-LUMO of the Co_4O_4 cluster using different amounts of HF exchange. Acetonitrile.[a]

%HF	Del [b]		IE (eV)	$E^0(1)$ [c]	Loc [d]				IE (eV)	$E^0(1)$ [c]
	Co(d)[e]	*O(p)*[e]			*Co(d)*[e]	*O(p)*[e]	*Co(d)*[f]	*Co(d)*[g]		
0	70.8	19.3	4.63	0.19	24.8	19.5	45.2	70.0	5.02	0.58
5	69.0	21.1	4.86	0.42	28.1	21.1	40.3	68.4	5.14	0.70
10	66.7	23.2	5.12	0.68	30.8	22.7	36.4	67.2	5.29	0.85
15[h]	**63.8**	**26.6**	**5.41**	**0.97**	**61.8**	**17.5**	**10.5**	**72.3**	5.42	0.98
20	60.4	28.4	5.70	1.26	73.1	12.7	4.6	77.7		
25	55.9	31.3	6.00	1.56	77.4	10.1	3.4	80.7	5.51	1.07

[a] BP86/6-311G(d) optimized geometries. [b] Delocalized geometric and electronic structure. [c] V vs. NHE. [d] Localized geometric and electronic structure. [e] BP86(XXHF)/6-311+G(d)/6-31G(d) population analyses; total d or p characters are given. [f] 'Spectator Co(III)' contribution. [g] Total Co(d) character including 'spectator Co(III)'. [h] Bolded values used in manuscript.

Table S6. Optimized bond distances of the oxidized states of CoM_3O_4 models.

	$CoAl_3$	**$CoGa_3$**	**$CoSc_3$**
Co(1)-M(2)	2.847	2.915	3.038
M(3)-M(4)	3.007	3.142	3.283
Co(1)-M(4)	2.708	2.784	2.861
Co(1)-M(3)	2.725	2.800	2.857
M(2)-M(4)	2.768	2.869	3.045
M(2)-M(3)	2.759	2.861	3.044
Co(1)-N	1.988	1.998	1.990
M(2)-N	2.074	2.108	2.372
M(3)-N	2.070	2.101	2.352
M(4)-N	2.074	2.105	2.359
Co(1)-OAc(1)	1.965	1.964	1.954
Co(1)-OAc(2)	1.975	1.975	1.963
Co(1)-O(1)	1.863	1.865	1.875
Co(1)-O(2)	1.862	1.862	1.865
Co(1)-O(3)	1.820	1.814	1.821
M(2)-OAc(1)	1.950	2.054	2.163
M(2)-OAc(2)	1.945	2.059	2.149
M(2)-O(1)	1.907	1.996	2.075
M(2)-O(2)	1.909	2.006	2.088
M(3)-OAc(1)	1.928	2.034	2.145
M(3)-OAc(2)	1.932	2.027	2.138
M(3)-O(1)	1.923	2.016	2.073
M(3)-O(2)	1.912	1.997	2.072
M(4)-OAc(1)	1.923	2.027	2.145
M(4)-OAc(2)	1.933	2.023	2.123
M(4)-O(1)	1.941	2.032	2.092
M(4)-O(2)	1.904	1.990	2.055

Table S7. Relative stabilization energies of neutral and oxidized states as a function of dielectric constant. Ionization energies are given at the bottom of the table. All values are given in eV.

neutral	**Co_4O_4**	**$CoAl_3$**	**$CoGa_3$**	**$CoSc_3$**
dielectric constant				
0	0.000	0.000	0.000	0.000
2	–0.399	–0.393	–0.416	–0.418
4	–0.726	–0.716	–0.756	–0.753
6	–0.871	–0.859	–0.907	–0.900
35.69	–1.174	–1.159	–1.222	–1.206
oxidized	**Co_4O_4**	**$CoAl_3$**	**$CoGa_3$**	**$CoSc_3$**
dielectric constant				
0	**0.000**	0.000	0.000	0.000
2	**–0.782**	–0.748	–0.757	–0.769
4	**–1.239**	–1.176	–1.192	–1.206
6	**–1.410**	–1.334	–1.353	–1.367
35.69	**–1.728**	–1.624	–1.648	–1.662
IEs	**Co_4O_4**	**$CoAl_3$**	**$CoGa_3$**	**$CoSc_3$**
dielectric constant				
0	5.960	5.458	5.583	5.754
2	5.577	5.191	5.242	5.403
4	5.448	5.086	5.148	5.301
6	5.421	5.070	5.137	5.287
35.69	5.406	5.080	5.157	5.298

C. Figures

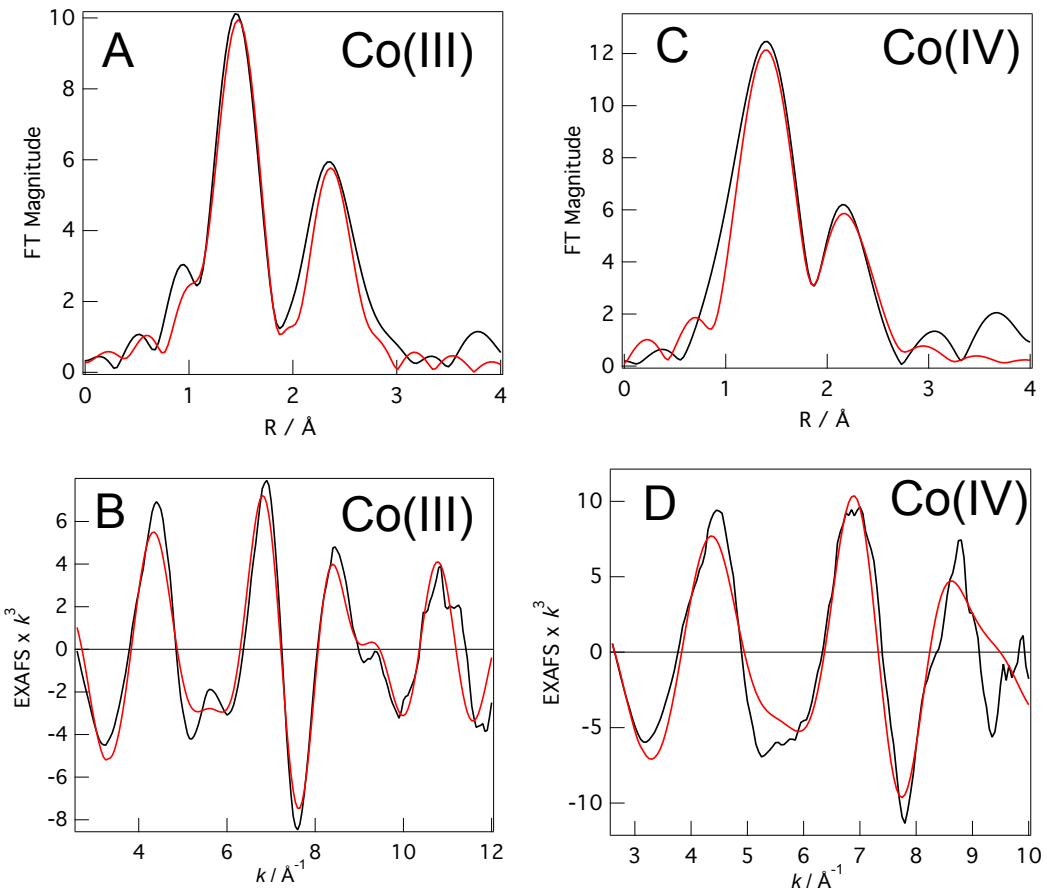

Figure S1. Co K-edge EXAFS fits (red lines) to experimental data (black lines) for the Co(III) (left) and Co(IV) states (right). (A) and (C) Fourier transforms and (B) and (D) k^3-weighted EXAFS oscillations.

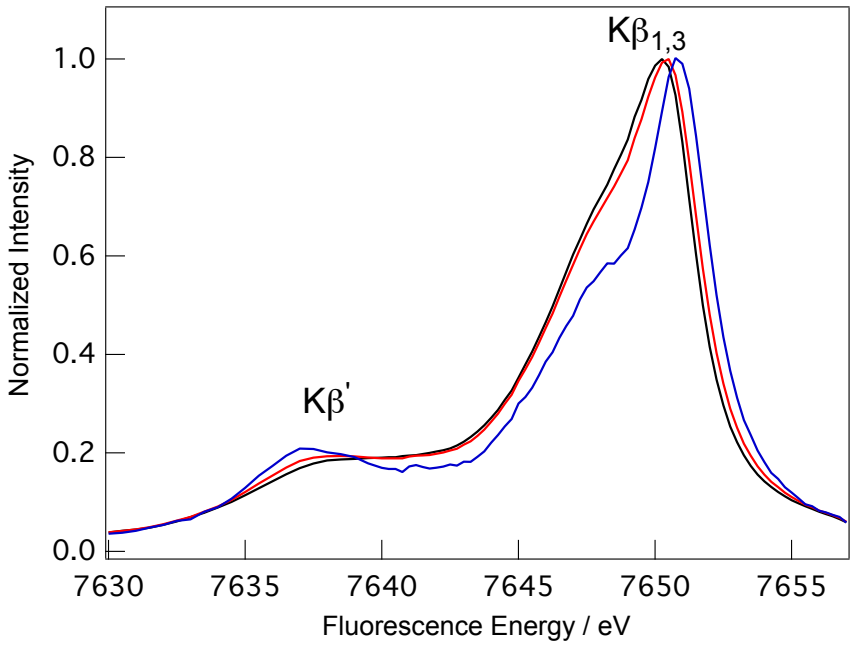

Figure S2. Co Kβ X-ray emission spectra (hν = 7730 eV) of the neutral cubane (black line), oxidized cubane (red line), and the Co(IV) spectrum (blue line).

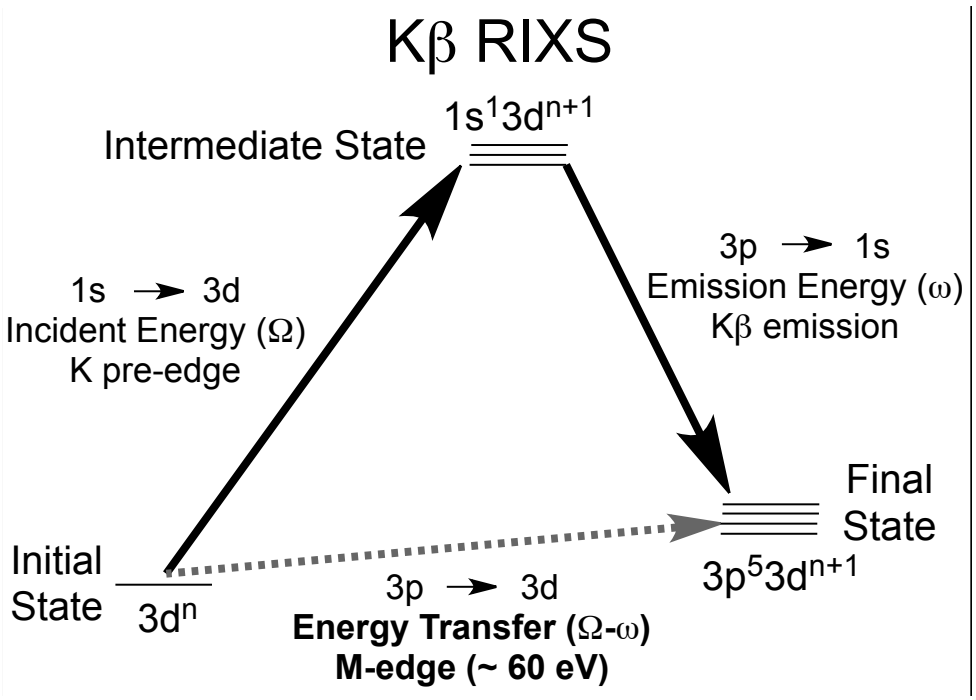

Figure S3. General outline of the absorption and emission process involved in 1s3p (Kβ) RIXS. The incident energy induces 1s absorption from the initial $3d^n$ to intermediate $1s^13d^{n+1}$ intermediate state. This is followed by Kβ emission to the $3p^53d^{n+1}$ final state. The overall two-photon process accesses the same initial and final states as in 3p → 3d absorption, which corresponds to the metal M-edge (~60 eV for Co).

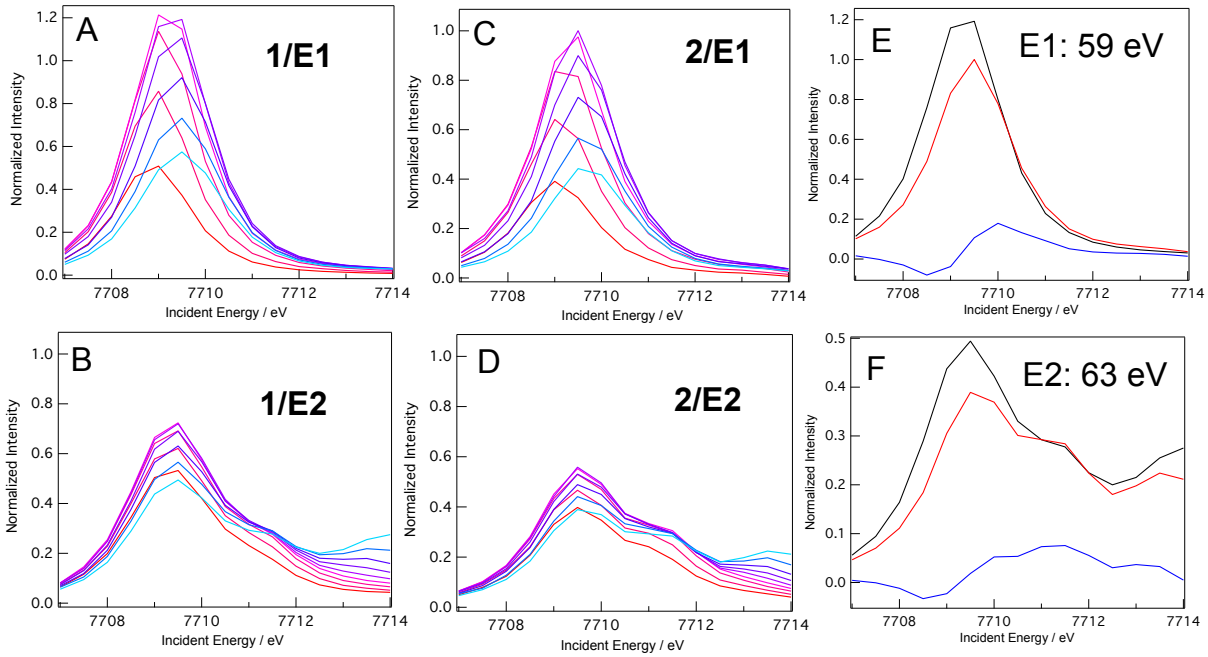

Figure S4. Constant final state (CFS) cuts of **1** (A and B) and **2** (C and D). (A) and (C), resonant with E1 (energy transfers ~58 – 60 eV); (B) and (D), resonant with E2 (energy transfers ~61 – 63 eV). CFS cuts through E1 (E) and E2 (F) of **1** (black line), **2** (red line), and Co(IV) (blue line).

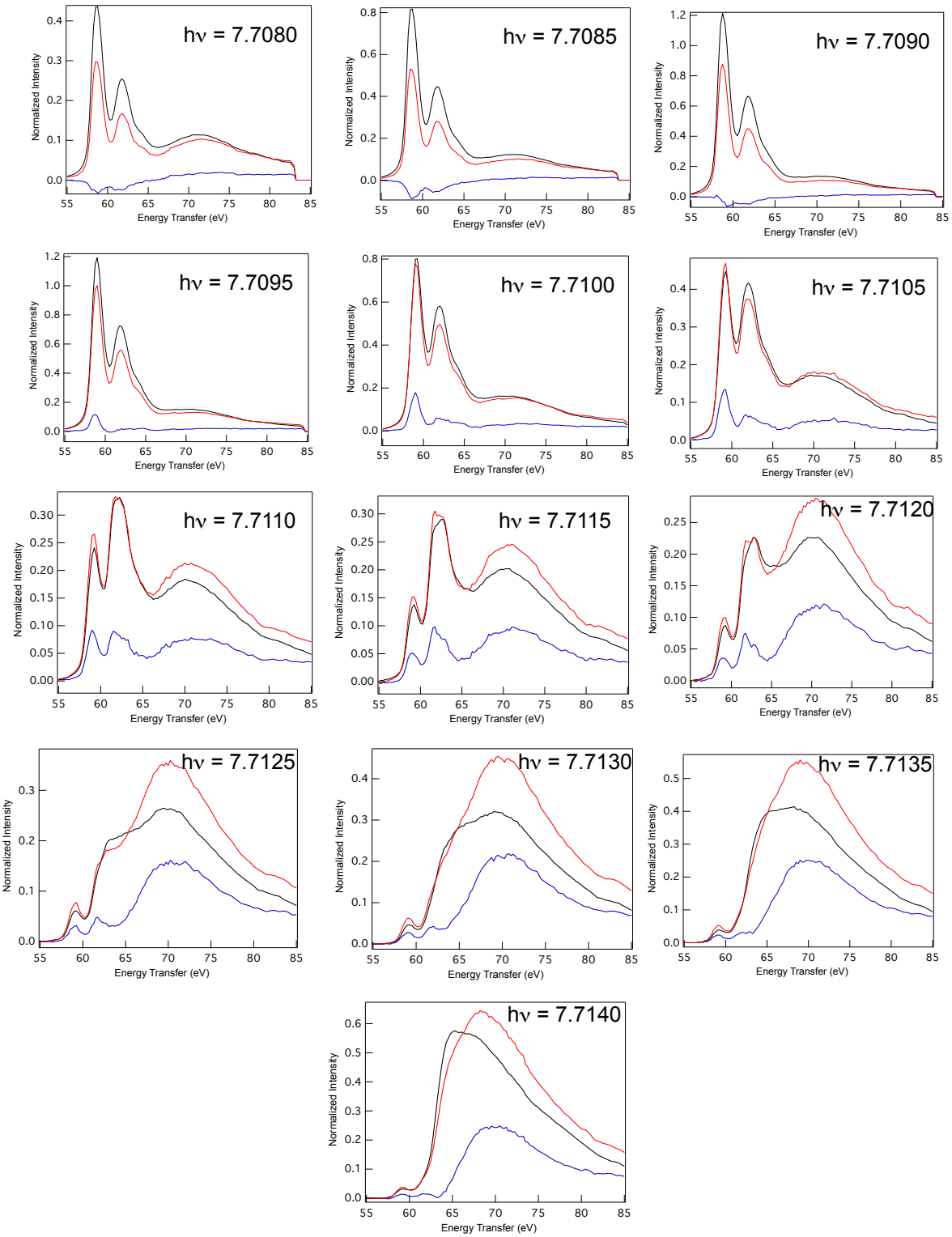

Figure S5. Constant incident energy cuts of the neutral cubane (black line), oxidized cubane (red line), and Co(IV) (blue line).

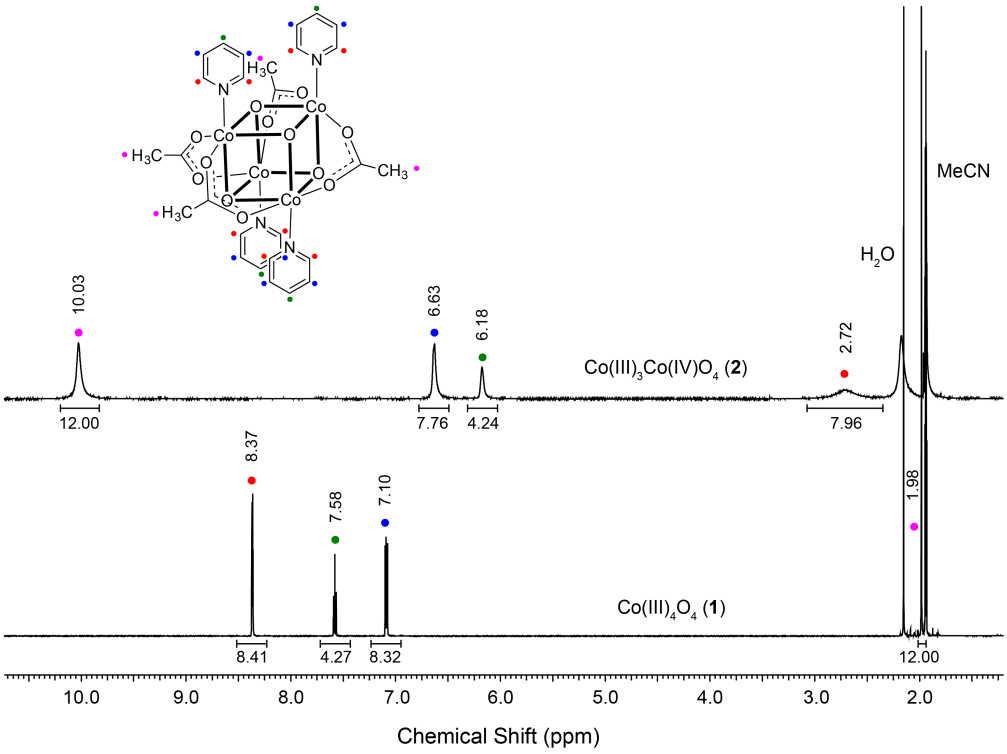

Figure S6. Nuclear magnetic resonance (^{1}H NMR) spectra of compounds **1** ($Co(III)_4O_4$) and **2** ($Co(III)_3(IV)O_4$) in CD_3CN, with peak assignments given by colored circles. The spectrum of **2** shows broadened and shifted peaks due to the paramagnetic nature of the S = ½ core. Both spectra are consistent with published spectra.[1] Mass spectrometry of **1** shows peaks at *m*/*z* = 852.95 and 773.90, assigned to $[Co_4O_4py_4OAc_4\text{-}H]^+$ and $[Co_4O_4py_3OAc_4\text{-}H]^+$, respectively. Mass spectrometry of **2** also showed peaks at *m*/*z* = 852.95 and 773.90, in addition to a new peak at 366.95, assigned to $[Co_4O_4py_3OAc_4\text{-}H]^{2+}$. Some of **2** is reduced to **1** in the ionizing conditions of the mass spectrometry chamber, but the 2+ peak at 366.95 confirms the presence of a singly oxidized compound, consistent with the NMR result.

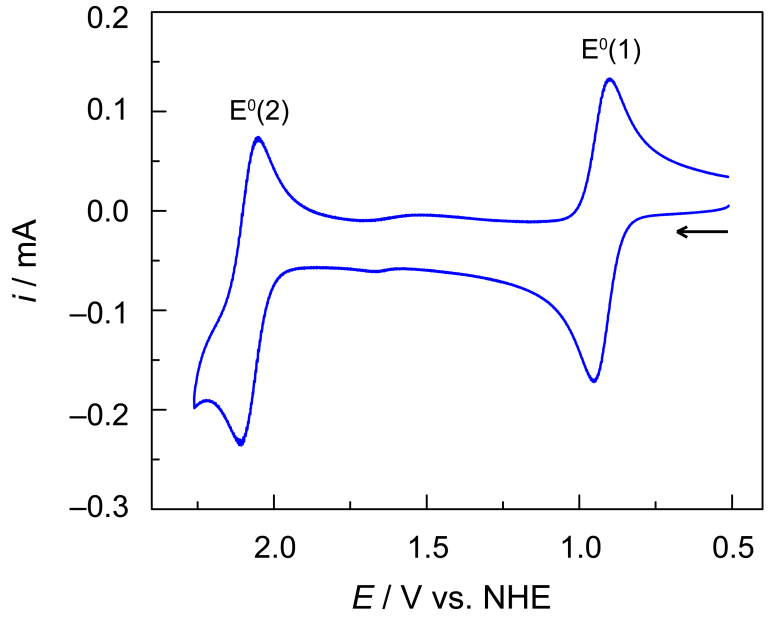

Figure S7. Cyclic voltammogram (CV) of **1** in MeCN + 0.1 M *n*-Bu_4NPF_6 under N_2 on a glassy carbon electrode, at scan rate v = 0.1 V/s. The standard potentials of the first and second oxidation were determined by averaging the anodic and cathodic peaks: $E^0(1)$ = 0.94 V and $E^0(2)$ = 2.09 V vs. NHE.

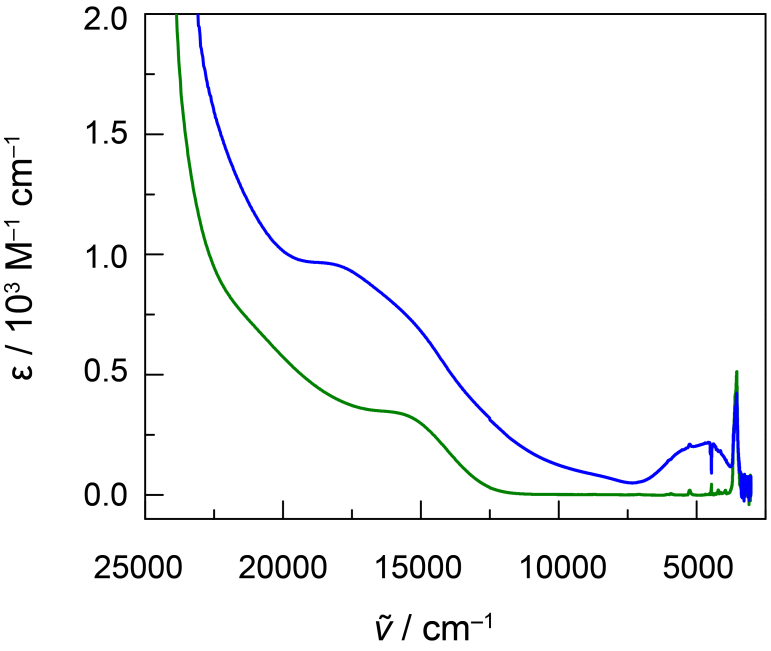

Figure S8. Room-temperature UV-vis-nIR absorption spectra of **1** $(Co(III)_4O_4$, green trace) and **2** $(Co(III)_3Co(IV)O_4$, blue trace); 2.5 mM solutions of each were prepared in deuterated acetonitrile. Solvent overtones in the low-energy region are too intense for an accurate background subtraction. An intervalence charge transfer (IVCT) band centered at 4580 cm^{-1} in the absorption spectrum of **2** allows for a bandwidth analysis and Robin-Day classification as follows:[17,18,19]

The experimental bandwidth at half height, $\Delta\nu_{1/2} = 2267\ \mathrm{cm}^{-1}$, is narrower than the theoretical width, $\Delta\nu_{1/2}^{0} = \sqrt{16\mathrm{RTln}(2)\nu_{\max}} = 3253\ \mathrm{cm}^{-1}$. The ratio between experimental and theoretical bandwidths yields the parameter $\Gamma = 1 - \left(\Delta\nu_{1/2}\right)/\left(\Delta\nu_{1/2}^{0}\right) = 0.303$, which classifies compound **2** as a Robin-Day Class II mixed-valence compound $(0 < \Gamma < 0.5)$. In addition, the lower and upper bounds for the electronic coupling factor H_{ab} can be estimated. The lower limit is given by $H_{\mathrm{ab}} = 0.0206\sqrt{\nu_{\max}\varepsilon_{\max}\Delta\nu_{1/2}}/r_{ab} = 352\ \mathrm{cm}^{-1}$, taking the value of $r_{\mathrm{ab}} = 2.786\ \text{Å}$ as the average of the four Co-Co bonds in the crystal structure of **2**.[1]

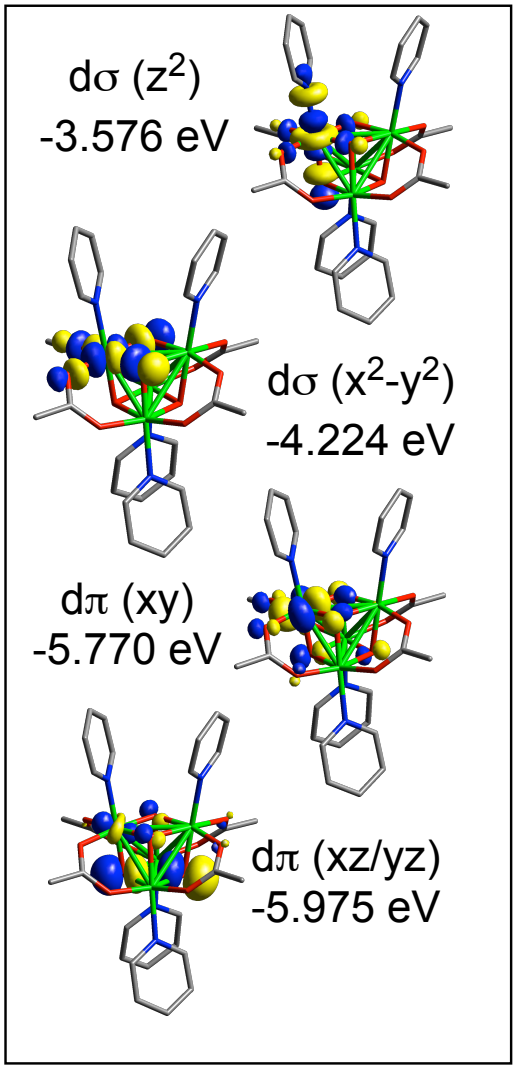

Figure S9. The β-LUMOs of formally S = 1 Co(V) in doubly oxidized $CoAl_3O_4$.

DFT Structures

Neutral Co_4O_4

Co	–0.92162300	1.08668300	–0.91777900
Co	–0.91972000	–1.08147300	0.92648600
Co	0.91789000	–0.92430100	–1.08204400
Co	0.92746800	0.92335100	1.08083100
O	–0.92870400	0.79148800	0.92998300
O	–0.93777900	–0.78635300	–0.92088600
O	–0.74646700	1.11485900	–2.87423000
O	–0.72873800	–1.11822400	2.88073400
O	0.74136700	2.87508500	1.11925700
O	–0.72682700	3.01895500	–0.64933100
N	–2.83317700	1.31026100	–1.03426300
N	–2.83089800	–1.29146900	1.05911600
C	0.02070200	–0.28831900	3.50206700
C	0.07430700	–0.45410300	5.01501200
C	–0.02199200	0.26629600	–3.50016600
C	–0.07914300	0.33964700	–5.02027200
C	–3.47674900	2.00712400	–0.06547400
H	–2.85244200	2.31055700	0.77598100
C	–4.83999400	2.29317500	–0.13513900
H	–5.31088800	2.86293200	0.67042300
C	–5.57887800	1.84546900	–1.23706400
H	–6.64763200	2.06321200	–1.32138600
C	–4.91588600	1.11121700	–2.22763700
H	–5.44642100	0.73348600	–3.10584000
C	–3.55061600	0.85965700	–2.09089800
H	–2.98075300	0.31030200	–2.84005200
C	–3.53453900	–0.81857600	2.11539500
H	–2.95366500	–0.25906400	2.84852800
C	–4.90063000	–1.05619400	2.26802800
H	–5.42008200	–0.66079500	3.14507300
C	–5.57911300	–1.79839300	1.29397900
H	–6.64893600	–2.00530900	1.39100100
C	–4.85472100	–2.26721100	0.19120200
H	–5.33840000	–2.84301000	–0.60240500
C	–3.48966400	–1.99470800	0.10553800
H	–2.87626100	–2.31524100	–0.73739100
C	0.01309400	3.50191800	0.27482000
C	0.05465000	5.02163500	0.36056900
H	0.78421900	5.40417300	–0.37300000
H	0.36717700	5.34579700	1.36209000
H	–0.92516700	5.44835200	0.10413400
O	0.72404700	–0.65244900	–3.01632800
O	0.74797700	0.64440400	3.01619400
O	0.93725900	–0.92561000	0.79053000
O	0.93540500	0.92455300	–0.79192000
O	–0.73734800	–3.01423700	0.65242700
O	0.72361500	–2.87528800	–1.12253200
N	2.82502700	–1.10075800	–1.26302300
N	2.83724200	1.09591300	1.25073900
C	3.49517200	–2.01443400	–0.51954800

H	2.89012400	−2.54732200	0.21442300
C	4.86072100	−2.24809000	−0.68065000
H	5.35341900	−3.00151800	−0.06025600
C	5.57378700	−1.51242300	−1.63514300
H	6.64374000	−1.68102600	−1.78826300
C	4.88381700	−0.55325400	−2.38621700
H	5.39443200	0.05476600	−3.13787100
C	3.51779100	−0.37142000	−2.17055500
H	2.92986900	0.35630000	−2.72993700
C	3.53429200	0.36898400	2.15690600
H	2.94820500	−0.35312300	2.72504400
C	4.90200000	0.54822200	2.36349600
H	5.41552400	−0.05778400	3.11478600
C	5.58964100	1.50273800	1.60452300
H	6.66086200	1.66955100	1.75053900
C	4.87226100	2.23652100	0.65184100
H	5.36267900	2.98689200	0.02597800
C	3.50528800	2.00522400	0.50000700
H	2.89741400	2.53705000	−0.23223800
C	−0.01784200	−3.49863200	−0.28695900
C	−0.06946400	−5.01134600	−0.45326800
H	−0.77931100	−5.26104400	−1.25969600
H	−0.40988600	−5.49318500	0.47272900
H	0.91493800	−5.39929100	−0.75122400
H	0.88433900	0.04570300	−5.45954800
H	−0.83907900	−0.37152200	−5.38615400
H	−0.36246700	1.34813800	−5.35018600
H	0.43158100	0.46630100	5.49529200
H	−0.91301100	−0.73524500	5.40847400
H	0.76991100	−1.27346800	5.26312200

Oxidized Co_4O_4 (delocalized)

Co	−0.89752300	1.06829600	−0.94732600
Co	−0.89626000	−1.06522200	0.95319200
Co	0.89445300	−0.95285700	−1.06465900
Co	0.90414200	0.95068200	1.06314600
O	−0.94656800	0.80171000	0.89964100
O	−0.95604500	−0.79853100	−0.89304800
O	−0.72598500	1.05775600	−2.88508800
O	−0.71107600	−1.06096900	2.88929200
O	0.72169400	2.88553400	1.06345100
O	−0.70965300	2.98924500	−0.72840000
N	−2.82703300	1.31156100	−1.09672500
N	−2.82542500	−1.29406200	1.11796500
C	0.01967900	−0.20719000	3.50430100
C	0.07006500	−0.33181700	5.01297000
C	−0.01865200	0.18666200	−3.50337200
C	−0.07061400	0.23157300	−5.01650700
C	−3.47218800	2.04688200	−0.16092200
H	−2.86040100	2.38546400	0.67558500
C	−4.83256800	2.33981600	−0.25741200
H	−5.30849300	2.94548600	0.51746500
C	−5.55847400	1.85585900	−1.35165100

H	−6.62337000	2.07987100	−1.45855700
C	−4.89196900	1.08098200	−2.30700900
H	−5.41435800	0.67820800	−3.17798200
C	−3.52935400	0.82786800	−2.14636600
H	−2.95881000	0.24789000	−2.87078000
C	−3.51481200	−0.78213300	2.16294600
H	−2.93398800	−0.18851300	2.86808700
C	−4.87811200	−1.02051100	2.33986800
H	−5.39005000	−0.59534300	3.20639600
C	−5.55911000	−1.80870200	1.40577300
H	−6.62495000	−2.02129500	1.52577700
C	−4.84690600	−2.31958200	0.31481200
H	−5.33474000	−2.93562700	−0.44430800
C	−3.48485100	−2.04102300	0.20185900
H	−2.88330600	−2.40237900	−0.63234300
C	0.01124300	3.50464300	0.19574500
C	0.04429700	5.01774400	0.25171300
H	0.70867200	5.39163300	−0.54469100
H	0.42483100	5.36266400	1.22114500
H	−0.95617800	5.42969600	0.06008000
O	0.70868100	−0.73165400	−2.98716500
O	0.72975100	0.72387500	2.98673500
O	0.95549800	−0.89732800	0.80148200
O	0.95409600	0.89516700	−0.80314800
O	−0.71973100	−2.98675700	0.73136400
O	0.70602200	−2.88703800	−1.06506900
N	2.81931600	−1.15243700	−1.27113900
N	2.83162500	1.14748000	1.25948700
C	3.48706500	−2.07975500	−0.54655400
H	2.89092200	−2.62879200	0.18208900
C	4.84952700	−2.31948200	−0.72559300
H	5.34389400	−3.08615600	−0.12430200
C	5.55305100	−1.57642000	−1.68008400
H	6.61882400	−1.75197600	−1.84991900
C	4.86324000	−0.60402300	−2.41263300
H	5.36829300	0.00582300	−3.16546300
C	3.50050800	−0.41685800	−2.17954000
H	2.91504800	0.32188600	−2.72634300
C	3.51692100	0.41636800	2.16837900
H	2.93357900	−0.31726400	2.72391900
C	4.88098600	0.60281200	2.39368400
H	5.38883400	−0.00352900	3.14745500
C	5.56829200	1.57069300	1.65301000
H	6.63500600	1.74612900	1.81692700
C	4.86072100	2.30978900	0.69843200
H	5.35271000	3.07339800	0.09133800
C	3.49727000	2.07024000	0.52708700
H	2.89863000	2.61662100	−0.20135100
C	−0.01639200	−3.50363400	−0.20538600
C	−0.06428100	−5.01224100	−0.32939500
H	−0.80966300	−5.28477900	−1.09494800
H	−0.36141900	−5.46958600	0.62284500
H	0.90660200	−5.40309400	−0.66244700
H	0.89073500	−0.07919500	−5.44714100

H	–0.83519600	–0.48057300	–5.36908700
H	–0.34554100	1.23546700	–5.36483800
H	0.37359700	0.61849600	5.47013900
H	–0.90105300	–0.65969900	5.40772300
H	0.81108000	–1.10243100	5.28355000

Oxidized Co_4O_4 (localized)

Co	–0.92078100	0.30325800	–1.37891700
Co	–0.92161100	–0.27904300	1.38046400
Co	0.88204900	1.37777700	0.28293700
Co	0.88128500	–1.39712100	–0.28654700
O	–0.95185800	–1.15732700	–0.24579900
O	–0.92471900	1.21415300	0.25514600
O	0.76819700	2.89452100	–0.87723200
O	–0.74117600	–0.83975700	–2.90466800
O	–0.71592100	0.87145200	2.93471100
O	0.93697400	–0.21720600	1.16954100
O	–0.71022700	1.97741400	–2.34243200
O	0.70048700	–2.32250900	–1.95433200
O	0.93856900	0.26852600	–1.16048100
O	0.77120200	2.28863100	1.96522700
O	0.68836000	–2.91398600	0.85364300
O	–0.74105300	–1.93103000	2.32165900
N	–2.83830400	–0.35456800	1.61921300
N	–2.83753300	0.38207500	–1.61790700
N	2.85792700	1.66682100	0.26603600
N	2.82513600	–1.69203700	–0.27185900
C	–3.51533300	–0.68254700	–2.07212900
H	–2.92903800	–1.58135000	–2.22541300
C	3.54165600	1.99094200	1.37038700
H	2.96025800	2.04868200	2.28455300
C	–3.48828900	–1.49646300	1.34275100
H	–2.88229200	–2.28479900	0.91321500
C	3.49127600	1.59943900	–0.91225300
H	2.87058000	1.31308000	–1.76060000
C	0.00880900	–2.66719100	–4.19376300
H	0.26655900	–3.70986900	–4.00307200
H	0.77402800	–2.23480700	–4.85474700
H	–0.94972300	–2.59208600	–4.71341800
C	–0.02187300	–1.88204500	–2.90585600
C	–4.88141600	0.60282700	2.39977500
H	–5.39291500	1.46153400	2.82307000
C	–4.87529500	–0.62714200	–2.34230500
H	–5.38246400	–1.50917300	–2.72096700
C	4.84967400	1.86201300	–1.02691300
H	5.32703600	1.80292600	–2.00244000
C	0.03570900	2.91287600	–1.91563800
C	3.50644100	–2.02456400	–1.38046800
H	2.92108000	–2.06709200	–2.29636100
C	–5.55661800	–0.58213900	2.12972700
H	–6.61866700	–0.67485900	2.34189800
C	0.03109400	1.87922700	2.92798100
C	–0.02583200	–2.88897100	1.89727600

C	–4.85602700	1.66198300	–1.63769500
H	–5.34663100	2.61277700	–1.45079000
C	5.56953600	2.20516000	0.11658000
H	6.63367400	2.42500900	0.05617900
C	–3.49494900	1.53261100	–1.39490400
H	–2.89323800	2.35271400	–1.01220000
C	–5.55872100	0.56573000	–2.12721500
H	–6.62222700	0.64064200	–2.33927700
C	–3.52297400	0.67889900	2.12833700
H	–2.94591700	1.57178800	2.33044100
C	3.47353100	–1.65457600	0.89994700
H	2.87073500	–1.36831800	1.75415700
C	–0.00101900	–4.13103100	2.75026800
H	0.22816200	–5.00950500	2.14236700
H	–0.94927400	–4.25706000	3.27473100
H	0.78505200	–4.02193600	3.50457300
C	–4.84705900	–1.64697800	1.58550200
H	–5.33131600	–2.59074200	1.35522200
C	5.53570800	–2.29697000	–0.13796700
H	6.59411500	–2.54355100	–0.08278500
C	4.86258500	–2.33203900	–1.35523800
H	5.37010500	–2.60478800	–2.27836100
C	4.90151700	2.26638000	1.33628300
H	5.41718500	2.53268300	2.25469300
C	4.82543500	–1.94915800	1.00840100
H	5.30624200	–1.91454100	1.98100200
C	0.11269300	2.70073800	4.18815200
H	0.19156500	3.76268900	3.94995100
H	1.01798300	2.41421300	4.74055100
H	–0.75055300	2.50698200	4.82584200
C	0.07977300	4.19487100	–2.70546800
H	–0.21564100	5.03355400	–2.06307700
H	–0.57889700	4.13492600	–3.57307600
H	1.10757500	4.38836700	–3.02977700

Neutral $CoAl_3O_4$

Co	0.87569600	–0.88891300	–1.10161100
Al	–0.91147200	–1.11734900	0.88862700
Al	0.89478700	0.85403700	1.15845900
Al	–0.88163800	1.13916500	–0.83400600
O	0.96684900	–1.00386300	0.78830500
O	0.99509000	0.96881400	–0.73725900
O	0.65284900	–0.51543000	–3.03371400
O	0.77112300	0.42790400	3.09374400
O	–0.80330200	–3.04165700	0.52695300
O	0.63988300	–2.84060600	–1.24321300
N	2.76762300	–1.12301500	–1.29625000
N	2.94523100	1.18437600	1.46198200
C	–0.02449100	–0.46220800	3.55037400
C	–0.10898200	–0.58856500	5.06277200
C	–0.09603300	0.41253500	–3.47220000
C	–0.18109100	0.56039700	–4.98451900
C	3.42060400	–1.95649100	–0.44712300

H	2.80034000	−2.36022300	0.35448700
C	4.78160000	−2.23316200	−0.57884200
H	5.26034700	−2.91510000	0.12945200
C	5.50938100	−1.63438900	−1.61500600
H	6.57566000	−1.84212900	−1.74563500
C	4.83562700	−0.76295000	−2.48038200
H	5.35527100	−0.26630200	−3.30466800
C	3.47373400	−0.52833400	−2.28889200
H	2.89550200	0.12667600	−2.94078200
C	3.61640400	0.91492800	2.60212500
H	3.01123000	0.49233000	3.40608000
C	4.98153800	1.17299300	2.74551400
H	5.48121500	0.93904600	3.68916400
C	5.68034900	1.73298800	1.67041700
H	6.75013000	1.94896400	1.75288500
C	4.98492300	2.01117000	0.48867000
H	5.48896400	2.44548900	−0.37826200
C	3.61998700	1.72470300	0.42137900
H	3.00682800	1.89374100	−0.46953100
C	−0.09130800	−3.50051800	−0.43765300
C	−0.13968000	−5.00736000	−0.64276300
H	−1.16574500	−5.30835300	−0.90977100
H	0.11103400	−5.51924800	0.29955500
H	0.54994000	−5.32148900	−1.43652200
O	−0.80131700	1.24281400	−2.78812800
O	−0.77811600	−1.23526700	2.86779100
O	−0.98736400	0.77997700	1.03145200
O	−1.02392300	−0.73874800	−0.94867200
O	0.79159100	2.82972200	1.26980400
O	−0.66024400	3.08255500	−0.47384000
N	−2.92221900	1.64157500	−0.97308200
N	−2.97184600	−1.50665600	1.07263100
C	−3.57328200	1.83649100	0.19748700
H	−2.94892600	1.65677600	1.08098500
C	−4.91509800	2.22153600	0.24389800
H	−5.40152300	2.36974600	1.21151300
C	−5.61029700	2.41315900	−0.95575500
H	−6.66170600	2.71753000	−0.94961900
C	−4.93387000	2.21304200	−2.16448400
H	−5.43305600	2.35657600	−3.12638300
C	−3.59056900	1.83045300	−2.13115800
H	−2.99696900	1.67447900	−3.03442700
C	−3.65039400	−1.57444300	2.23726000
H	−3.05017400	−1.39912100	3.13244500
C	−5.01594700	−1.86527100	2.29124100
H	−5.52269000	−1.91369800	3.25865600
C	−5.70512400	−2.09797900	1.09570900
H	−6.77419300	−2.33237100	1.10547400
C	−5.00007300	−2.03058300	−0.11153700
H	−5.49591200	−2.20656400	−1.06957800
C	−3.63556900	−1.73393100	−0.08451900
H	−3.01040000	−1.65425000	−0.98086100
C	0.07463100	3.52568800	0.47147700
C	0.12780000	5.03466500	0.64408900

H	0.87734900	5.44679900	−0.05280600
H	0.42653300	5.30190800	1.66646500
H	−0.84108900	5.48799700	0.39210700
H	−1.19307500	0.28123300	−5.32239900
H	−0.01993000	1.61088600	−5.27198100
H	0.54915800	−0.08699800	−5.48663100
H	−0.41628400	−1.60155800	5.35588300
H	0.84771600	−0.32607800	5.53516700
H	−0.86623700	0.12281800	5.43477800

Neutral $CoGa_3O_4$

Co	−0.85199900	−0.57136800	1.42529900
Ga	0.93411200	−1.39414100	−0.50857800
Ga	−1.00675400	0.43951400	−1.31189800
Ga	0.86804000	1.38876000	0.51591400
O	−1.02061000	−1.28137700	−0.32471200
O	−1.08044200	1.10956700	0.57010700
O	−0.59743400	0.34115700	3.16272900
O	−0.90108300	−0.64922700	−3.10999900
O	0.84779700	−3.18799100	0.53772000
O	−0.57303600	−2.37660900	2.15314100
N	−2.73693600	−0.76184000	1.74212700
N	−3.09589100	0.65594100	−1.70727300
C	−0.08755600	−1.61462500	−3.29604300
C	−0.04678300	−2.19903200	−4.70353100
C	0.13558700	1.36295400	3.35135500
C	0.23691500	1.86026000	4.78914100
C	−3.39623300	−1.82542000	1.21895000
H	−2.78754900	−2.46347500	0.57675500
C	−4.75258500	−2.04863900	1.45921800
H	−5.23836800	−2.92219500	1.01575700
C	−5.46568800	−1.15140700	2.26395100
H	−6.52756300	−1.30886400	2.47581800
C	−4.78419200	−0.04721200	2.79146400
H	−5.29283100	0.68522700	3.42462100
C	−3.42826900	0.11786000	2.50652400
H	−2.84422900	0.95052300	2.89828300
C	−3.75087900	0.10982500	−2.75201100
H	−3.13062000	−0.48178900	−3.42831200
C	−5.12034200	0.30437100	−2.94795000
H	−5.61595500	−0.15277300	−3.80830100
C	−5.82933400	1.08978400	−2.03185300
H	−6.90261800	1.26108100	−2.16039800
C	−5.14328100	1.65282900	−0.94973600
H	−5.65835300	2.27093200	−0.21028700
C	−3.77335400	1.41545400	−0.81942300
H	−3.16158500	1.80477000	0.00158100
C	0.14985200	−3.27306400	1.60890900
C	0.20347400	−4.61668600	2.32709500
H	1.22832500	−4.79606000	2.69088000
H	−0.03483100	−5.42677100	1.6204030
H	−0.49156200	−4.64032800	3.17623900
O	0.81194400	2.03049700	2.48679500

O	0.71809500	−2.13371300	−2.45113600
O	0.96846200	0.45979800	−1.25916400
O	1.04975900	−0.44283800	1.20481700
O	−0.96616700	2.41235600	−2.00320900
O	0.52103300	3.21341000	−0.45297800
N	2.90034600	2.05240100	0.45280500
N	3.01257400	−1.88125400	−0.62996700
C	3.51690600	1.92497500	−0.74300000
H	2.89533000	1.45230500	−1.51415300
C	4.82898700	2.36195200	−0.93963000
H	5.29793700	2.24491800	−1.92005800
C	5.51736000	2.94749300	0.12964400
H	6.54517500	3.30158700	0.00228500
C	4.86938900	3.07756700	1.36367100
H	5.36847200	3.53348600	2.22269300
C	3.55561500	2.61771400	1.48731100
H	2.97810300	2.69333300	2.41165100
C	3.63714100	−2.35889500	−1.72502900
H	3.00164000	−2.47714600	−2.60549800
C	4.99501600	−2.68866200	−1.71460300
H	5.46667800	−3.07812500	−2.62053500
C	5.72269000	−2.51705800	−0.53129600
H	6.78670200	−2.77029200	−0.49216700
C	5.06701800	−2.02143800	0.60208100
H	5.59738500	−1.87524800	1.54648500
C	3.70695000	−1.71538100	0.51688700
H	3.11261600	−1.32391100	1.35040600
C	−0.25870200	3.32541700	−1.45687300
C	−0.38905000	4.72157400	−2.05496000
H	−1.19504900	5.25978300	−1.52787000
H	−0.65668000	4.66697400	−3.11898700
H	0.53944100	5.29282600	−1.91794500
H	1.25281700	1.66263500	5.16993200
H	0.07946000	2.94908100	4.82678100
H	−0.48666800	1.34855700	5.43680000
H	0.27057800	−3.25057700	−4.68302900
H	−1.02273300	−2.10403200	−5.19945400
H	0.68606900	−1.62965500	−5.30034300

Neutral $CoSc_3O_4$

Co	0.73621000	−1.04078200	−1.20634400
Sc	−0.96141700	−1.17667600	1.01371100
Sc	1.18051400	0.89186500	1.09438000
Sc	−0.91288900	1.20526500	−0.99914500
O	1.01443100	−1.11998100	0.68324400
O	1.05349500	0.82896600	−0.96649900
O	0.44578300	−0.86234600	−3.14170400
O	1.09947800	0.32769600	3.23351400
O	−0.90776800	−3.28952100	0.43742000
O	0.45778900	−2.97042100	−1.36463600
N	2.60333300	−1.31225000	−1.49002900
N	3.54727600	1.14635900	1.45263600
C	0.22922300	−0.40941100	3.80679900

C	0.23111100	−0.43538600	5.33185900
C	−0.32318600	−0.02144100	−3.71872400
C	−0.48970600	−0.20372500	−5.22256800
C	3.27558800	−2.22343000	−0.74728900
H	2.68064800	−2.71665300	0.02093300
C	4.63606100	−2.47062100	−0.93628600
H	5.13601600	−3.21866500	−0.31511900
C	5.33349100	−1.75617500	−1.91770700
H	6.39862200	−1.93649400	−2.09146000
C	4.63625400	−0.80119100	−2.66810300
H	5.13515400	−0.21104100	−3.44171800
C	3.27661400	−0.60204700	−2.42502900
H	2.68129200	0.13155700	−2.96705400
C	4.16844600	0.72888000	2.57572300
H	3.51859600	0.24987900	3.31405900
C	5.53867600	0.90771700	2.78822700
H	5.99777700	0.55645500	3.71619900
C	6.29599800	1.54346100	1.79763800
H	7.37055900	1.70060300	1.93343200
C	5.65507200	1.97723000	0.63135200
H	6.20715600	2.47938100	−0.16737200
C	4.28040100	1.76047700	0.50026800
H	3.72543400	2.08311100	−0.38535600
C	−0.26152600	−3.68334800	−0.58387200
C	−0.34465300	−5.16460800	−0.93421700
H	−1.39005100	−5.42353000	−1.16801800
H	−0.05174300	−5.76863000	−0.06094000
H	0.29299300	−5.41138900	−1.79264100
O	−0.96282700	0.93706000	−3.17414600
O	−0.65935400	−1.10244600	3.21328600
O	−0.81785700	0.89102500	1.03529700
O	−1.17426400	−0.79618100	−0.94261300
O	1.21894500	3.06918500	0.87058400
O	−0.43464200	3.33883000	−0.65607300
N	−3.18020200	1.97802700	−1.00075200
N	−3.29535400	−1.55289400	1.42893000
C	−3.69507200	2.36690100	0.18563100
H	−3.04267700	2.19648400	1.04900100
C	−4.96554100	2.94004500	0.29699900
H	−5.34394000	3.24313700	1.27684000
C	−5.72911700	3.11628000	−0.86315300
H	−6.72584700	3.56527900	−0.80997900
C	−5.19715500	2.71148100	−2.09330100
H	−5.75925900	2.83335800	−3.02306700
C	−3.91817700	2.14704900	−2.11724000
H	−3.44299800	1.81751000	−3.04696700
C	−3.86267000	−1.60856500	2.65164500
H	−3.18620700	−1.41039300	3.48918000
C	−5.21574100	−1.90771900	2.83876500
H	−5.63316500	−1.94619900	3.84851800
C	−6.00988800	−2.15931400	1.71365700
H	−7.07183500	−2.39944500	1.82544600
C	−5.42336400	−2.10297000	0.44380600
H	−6.00729700	−2.29459100	−0.46030300

C	–4.06258600	–1.79805000	0.34435600
H	–3.53970300	–1.73783600	–0.61619600
C	0.46398100	3.78246500	0.12760200
C	0.67357900	5.29301500	0.16032700
H	1.25452000	5.59323800	–0.72834400
H	1.22721100	5.59934900	1.05808600
H	–0.29254600	5.81593700	0.10759500
H	–1.50766500	–0.57580100	–5.42632500
H	–0.38757200	0.76536200	–5.73445300
H	0.23535100	–0.92479000	–5.62132700
H	–0.11544900	–1.40839300	5.70793700
H	1.22745700	–0.20320100	5.73279600
H	–0.46656800	0.33633800	5.70014200

Oxidized $CoAl_3O_4$

Co	0.83487500	–0.69924500	–1.18747500
Al	–0.93060600	–1.29894600	0.77632500
Al	0.90788300	0.70564400	1.28720400
Al	–0.91620700	1.32814500	–0.68691000
O	0.96044500	–1.08444700	0.63060900
O	0.97607400	1.05833300	–0.58771200
O	0.64944800	–0.07091500	–3.05110500
O	0.73807700	0.01800700	3.10382500
O	–0.76162100	–3.09707600	0.10092300
O	0.65902600	–2.60802900	–1.62055500
N	2.78638100	–0.94403400	–1.47476800
N	2.93614600	0.98987200	1.61490800
C	–0.02666400	–0.94358500	3.45876700
C	–0.09077100	–1.27115900	4.93263200
C	–0.07753200	0.92482700	–3.37515900
C	–0.10221600	1.30720400	–4.83961800
C	3.44239800	–1.83146200	–0.69244500
H	2.83980500	–2.28198900	0.09755000
C	4.79670500	–2.11375500	–0.87528500
H	5.28680200	–2.84158800	–0.22431000
C	5.49815800	–1.45988700	–1.89453700
H	6.55818700	–1.66819200	–2.06485500
C	4.81540700	–0.53694800	–2.69429100
H	5.31840200	–0.00341400	–3.50432000
C	3.45998500	–0.30398400	–2.45528900
H	2.87143000	0.38365400	–3.06211800
C	3.59131100	0.58352500	2.72711600
H	2.98333700	0.05196300	3.46028600
C	4.94698300	0.84272000	2.93414500
H	5.42930400	0.49738300	3.85156100
C	5.65773400	1.55251000	1.96055900
H	6.71918800	1.77734600	2.09863700
C	4.98233200	1.97474000	0.80963600
H	5.49443300	2.53675700	0.02513100
C	3.62653000	1.67694900	0.67226500
H	3.03983000	1.97024700	–0.20175100
C	–0.03665500	–3.40993900	–0.91044300
C	–0.00812900	–4.87034000	–1.30573000

H	–1.03305200	–5.21647900	–1.51058500
H	0.36890000	–5.46936200	–0.46185700
H	0.62161400	–5.03254200	–2.18843200
O	–0.79741800	1.63506000	–2.58153800
O	–0.76529600	–1.63519800	2.67186300
O	–0.99875300	0.58962200	1.06589800
O	–0.97321900	–0.58488100	–1.00898000
O	0.73841200	2.60447400	1.67433400
O	–0.66605300	3.13095200	–0.03571300
N	–2.93847900	1.77852600	–0.77157600
N	–2.95937800	–1.70161800	0.85749300
C	–3.62370100	1.79269000	0.39866200
H	–3.04234300	1.47581200	1.26834800
C	–4.96106800	2.18189300	0.47476500
H	–5.46881000	2.18204300	1.44211400
C	–5.62310200	2.57344500	–0.69458200
H	–6.66981400	2.88940300	–0.66445100
C	–4.91709000	2.56137800	–1.90238800
H	–5.38863100	2.86626500	–2.83954400
C	–3.57958500	2.16277400	–1.90120200
H	–2.97244400	2.15394000	–2.80751000
C	–3.63191100	–1.93852500	2.00798900
H	–3.03754700	–1.87011800	2.92045500
C	–4.98777900	–2.26984600	2.02652600
H	–5.48482500	–2.45767600	2.98110700
C	–5.67903800	–2.36719200	0.81401000
H	–6.73971800	–2.63336600	0.79714000
C	–4.98459100	–2.12554100	–0.37714200
H	–5.48023300	–2.19541500	–1.34818700
C	–3.63039100	–1.79774100	–0.31615600
H	–3.03280200	–1.59906500	–1.20924800
C	0.04755200	3.43214500	0.98502600
C	0.09683900	4.88787700	1.38592600
H	0.83438500	5.40621900	0.75002300
H	0.40748400	4.99684800	2.43249500
H	–0.87528500	5.37008700	1.21552900
H	–1.12662500	1.19894900	–5.23031800
H	0.17516100	2.36672900	–4.95185400
H	0.57363900	0.67534200	–5.42812500
H	–0.41311100	–2.30781400	5.09299000
H	0.87713600	–1.08920700	5.41864100
H	–0.82524900	–0.60116300	5.41148400

Oxidized $CoGa_3O_4$

Co	–0.81798300	–0.51713600	1.40999200
Ga	0.95085600	–1.48788500	–0.50867900
Ga	–1.02658700	0.41544800	–1.34419200
Ga	0.89532900	1.49361000	0.48037100
O	–1.01708200	–1.27491500	–0.28247000
O	–1.07135800	1.10872900	0.53775000
O	–0.61180700	0.44722500	3.12061200
O	–0.86503700	–0.68221500	–3.07326700
O	0.80888400	–3.18495100	0.60322900

O	−0.58510800	−2.30190600	2.19615100
N	−2.76267800	−0.74540300	1.80806200
N	−3.08639800	0.64200200	−1.73320500
C	−0.08748000	−1.67951500	−3.25350300
C	−0.07372300	−2.29283800	−4.63929700
C	0.08600700	1.50131400	3.28659600
C	0.09207100	2.09683500	4.68137200
C	−3.41748000	−1.78747400	1.24802700
H	−2.82335400	−2.38678900	0.55667800
C	−4.76201100	−2.04435700	1.52054000
H	−5.25243100	−2.89956100	1.04948600
C	−5.45277600	−1.20142000	2.39820000
H	−6.50443100	−1.38467400	2.63612800
C	−4.77067100	−0.12071700	2.96835200
H	−5.26609500	0.56371900	3.66116400
C	−3.42610300	0.07717400	2.64912500
H	−2.83786900	0.88860300	3.07657100
C	−3.71719600	0.12084900	−2.80925700
H	−3.09220600	−0.47778100	−3.47356900
C	−5.07190000	0.35170500	−3.05389500
H	−5.54385800	−0.08438600	−3.93740000
C	−5.79586800	1.14943700	−2.16081800
H	−6.85690100	1.35238900	−2.33185800
C	−5.13793400	1.68806600	−1.04871700
H	−5.66365400	2.32051500	−0.32966000
C	−3.78213200	1.41444800	−0.86668600
H	−3.20125600	1.79781400	−0.02293200
C	0.10065600	−3.24292200	1.67038800
C	0.08439300	−4.57388300	2.39642000
H	1.10978300	−4.83969900	2.69746200
H	−0.26322200	−5.36171400	1.71034000
H	−0.56077400	−4.53621700	3.28229100
O	0.78660600	2.11968500	2.40485600
O	0.70271300	−2.20146700	−2.38962400
O	0.98515000	0.39393600	−1.17603100
O	0.97984300	−0.40698000	1.19300200
O	−0.89063400	2.31558500	−2.09850900
O	0.52172400	3.20367200	−0.53455000
N	2.91787700	2.07471600	0.45043300
N	3.00097300	−1.94295500	−0.57095800
C	3.58265600	1.90841400	−0.71743100
H	3.00769400	1.41253900	−1.50491100
C	4.89809000	2.34238100	−0.88291800
H	5.39981600	2.19378200	−1.84197000
C	5.54670400	2.96893800	0.18799900
H	6.57595900	3.32399000	0.08400100
C	4.85406900	3.14034700	1.39193000
H	5.31917100	3.62992800	2.25068200
C	3.53885700	2.68255500	1.48715600
H	2.93627600	2.79738600	2.38958400
C	3.61816700	−2.43810600	−1.66716500
H	2.98635200	−2.55281300	−2.54958200
C	4.96780700	−2.79440800	−1.65528900
H	5.42845200	−3.19779700	−2.56001700

C	5.70078700	−2.63535500	−0.47387500
H	6.75785600	−2.91308100	−0.43438200
C	5.05703800	−2.12187100	0.65855400
H	5.58988600	−1.98616300	1.60251400
C	3.70523200	−1.78860900	0.57413700
H	3.13923900	−1.38834000	1.41938100
C	−0.21918500	3.26992200	−1.57843500
C	−0.32288200	4.62886700	−2.24048700
H	−0.98016400	5.27227900	−1.63237200
H	−0.74546100	4.54531600	−3.24921000
H	0.66252600	5.11449200	−2.27368200
H	1.12529900	2.14312400	5.05953600
H	−0.28365600	3.13131900	4.64235000
H	−0.51946400	1.50209300	5.37055000
H	0.27888100	−3.33157900	−4.60770000
H	−1.06877900	−2.24014600	−5.10130100
H	0.61365700	−1.71059700	−5.27606200

Oxidized $CoSc_3O_4$

Co	−0.71925700	−0.57099800	1.42580300
Sc	0.99721600	−1.49372800	−0.66832500
Sc	−1.18648700	0.50791600	−1.37526600
Sc	0.94737100	1.56596700	0.52028800
O	−0.99520200	−1.25782900	−0.29743400
O	−1.04560600	1.08230000	0.62743200
O	−0.46935500	0.21824500	3.20553400
O	−1.09197700	−0.70942000	−3.16057800
O	0.89942000	−3.20398900	0.62214300
O	−0.48669000	−2.34479900	2.21053500
N	−2.65218900	−0.78852700	1.84724300
N	−3.52893200	0.65197100	−1.72084100
C	−0.27262500	−1.63484000	−3.47662700
C	−0.34865300	−2.23093700	−4.86662900
C	0.29540800	1.20826800	3.48046600
C	0.41951100	1.56685400	4.94800000
C	−3.31346600	−1.86282400	1.36401600
H	−2.73340300	−2.50731800	0.70315700
C	−4.65429600	−2.09824400	1.67109800
H	−5.15250400	−2.98155800	1.26475200
C	−5.33114500	−1.19660400	2.49989200
H	−6.37977100	−1.36116400	2.76323000
C	−4.64218300	−0.07887600	2.98349300
H	−5.12927300	0.65424600	3.63076900
C	−3.30162800	0.09415600	2.63504600
H	−2.71069900	0.93847300	2.98737300
C	−4.18120300	−0.05874300	−2.66870200
H	−3.56481400	−0.76070800	−3.23675900
C	−5.54556800	0.10016500	−2.92363400
H	−6.02663100	−0.49463300	−3.70394300
C	−6.26782500	1.03414900	−2.17207400
H	−7.33559300	1.18769400	−2.35269500
C	−5.59805000	1.77315000	−1.18961100
H	−6.12117000	2.51663800	−0.58325100

C	−4.23286200	1.55215400	−0.99679900
H	−3.66278700	2.10712100	−0.24634600
C	0.22973200	−3.27858300	1.70106900
C	0.26788600	−4.58212800	2.47404600
H	1.31187900	−4.82553200	2.72520400
H	−0.10626900	−5.39663800	1.83410300
H	−0.33026600	−4.52362100	3.39114000
O	0.95294800	1.90455200	2.63869700
O	0.61703300	−2.10138300	−2.68276700
O	0.85110800	0.49535000	−1.23067900
O	1.06990500	−0.43603400	1.11357800
O	−1.17262500	2.60151900	−1.85817700
O	0.41291500	3.37376000	−0.45539400
N	3.20366800	2.21411800	0.37809100
N	3.30044600	−1.96223600	−0.86972100
C	3.80875800	2.17763300	−0.83239700
H	3.21697400	1.73739100	−1.64086100
C	5.09890600	2.66933100	−1.04036000
H	5.54628300	2.62266600	−2.03620500
C	5.79308100	3.22154600	0.04302900
H	6.80322600	3.61967600	−0.08901600
C	5.17213500	3.25971800	1.29704500
H	5.67683600	3.68469600	2.16802300
C	3.87858700	2.74758400	1.42239000
H	3.34122200	2.75878300	2.37531600
C	3.85577100	−2.42530800	−2.01298200
H	3.18119800	−2.49545900	−2.87131200
C	5.19763100	−2.80399300	−2.09650400
H	5.60083900	−3.17731300	−3.04096900
C	5.99889900	−2.70242200	−0.95320000
H	7.05187700	−2.99651800	−0.98477600
C	5.42879400	−2.22411800	0.23287400
H	6.01696300	−2.13340400	1.14926900
C	4.07892700	−1.86731000	0.23289400
H	3.58044200	−1.49390800	1.13272300
C	−0.45271900	3.54079800	−1.38247200
C	−0.63399700	4.94178900	−1.92672100
H	−1.08312000	5.57832100	−1.14674300
H	−1.28156200	4.94488200	−2.81189900
H	0.34471500	5.38170600	−2.16949600
H	1.45210700	1.36985000	5.27874300
H	0.23461300	2.64289900	5.08586200
H	−0.27070200	0.97931900	5.56517200
H	−0.55763500	−3.31006800	−4.79495800
H	−1.12250700	−1.74290400	−5.47137900
H	0.62659400	−2.12958200	−5.36793600

References

(1) Ullman, A. M.; Liu, Y.; Huynh, M.; Bediako, D. K.; Wang, H.; Anderson, B. L.; Powers, D. C.; Breen, J. J.; Abruna, H. D.; Nocera, D. G. *J. Am. Chem. Soc.* **2014**, *136*, 17681.

(2) McCool, N. S.; Robinson, D. M.; Sheats, J. E.; Dismukes, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 11446.

(3) Berardi, S.; La Ganga, G.; Natali, M.; Bazzan, I.; Puntoriero, F.; Sartorel, A.; Scandola, F.; Campagna, S.; Bonchio, M. *J. Am. Chem. Soc.* **2012**, *134*, 11104.

(4) Ravel, B.; Newville, M. *J. Synch. Rad.* **2005**, *12*, 537.

(5) Shvyd'ko, Y. V.; Hill, J. P; Burns, C. A.; Coburn, D. S.; Brajuskovic, B. Casa, D.; Goetze, K.; Gog, T.; Khachatryan, R.; Kim, J.-H.; Kodituwakku, C. N.; Ramanathan, M.; Roberts, T.; Said, A.; Sinn, H.; Shu, D.; Stoupin, S.; Upton, M.; Wieczorek, M.; Yavas, H. *J. Elec. Spect. Rel. Phenom.* **2013**, *188*, 140.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.01; Gaussian, Inc.: Wallingford, CT, 2009.

(7) Tenderholt, A. L. QMForge, Version 2.1; Stanford University, Stanford, CA.

(8) Kieber-Emmons, M. T. β-LUMO, Version 0.9b; Burlingame, CA, **2011**.

(9) Perdew, J. P. *Phys. Rev. B.* **1986**, *33*, 8822.

(10) Becke, A. D. *Phys. Rev. A.* **1988**, *38*, 3098.

(11) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(12) Francl, M. M.; Pietero, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(13) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(14) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* **1998**, *109*, 1223.

(15) Miertus, S.; Scrocco, E.; Tomasi, *J. Chem. Phys.* **1981**, *55*, 117.

(16) Sarmah, P.; Chakrabarty, R.; Phukan, P.; Das, B. K. *J. Mol. Catal. A.: Chem.* **2007**, *268*, 36.

(17) Chakraborty, I.; Baran, P.; Sanakis, Y.; Simopoulous, A.; Fachini, E.; Raptis, R. G. *Inorg. Chem.*, **2008**, *47*, 11734.

(18) Gaudette, A. I.; Jeon, I.-R.; Anderson, J. S.; Grandjean, F.; Long, G. J.; Harris, T. D. *J. Am. Chem. Soc.* **2015**, *137*, 12617.

(19) Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168.